Phonon bottleneck in the low-excitation limit

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The phonon-bottleneck problem in the relaxation of two-level systems (spins) via direct phonon processes is considered numerically in the weak-excitation limit where the Schrödinger equation for the spin-phonon system simplifies. The solution for the relaxing spin excitation $p(t)$, emitted phonons $n_{\mathbf{k}}(t)$, etc. is obtained in terms of the exact many-body eigenstates. In the absence of phonon damping $\Gamma_{\rm ph}$ and inhomogeneous broadening, $p(t)$ approaches the bottleneck plateau $p_\infty > 0$ with strongly damped oscillations, the frequency being related to the spin-phonon splitting Δ at the avoided crossing. For any $\Gamma_{\rm ph} > 0$ one has $p(t) \to 0$ but in the case of strong bottleneck the spin relaxation rate is much smaller than $\Gamma_{\rm ph}$ and $p(t)$ is nonexponential. Inhomogeneous broadening exceeding Δ partially alleviates the bottleneck and removes oscillations of $p(t)$. The line width of emitted phonons, as well as Δ, increase with the strength of the bottleneck, i.e., with the concentration of spins.

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I. INTRODUCTION

Spin-lattice relaxation is an old an much studied problem that currently recieves a resurge of attention because of its vital importance in quantum information processing (see, e.g., Ref. 1 and references therein). Theoretical description of the spin-lattice relaxation as a single-spin process is in many cases insufficient because of the collective effects of incoherent and coherent nature, such as the phonon bottleneck[2] and superradiance,[3] respectively.

The problem of phonon bottleneck (PB) in relaxation of two-level systems (henceforth spins) via direct phonon emission/absorption processes, first recognized by Van Vleck[2] in 1941, remains unsolved until now. In two words, if the emitted phonons have nowhere to go, they are absorbed by spins again and thus the spins cannot relax efficiently. However transparent this picture might appear, is not easy to propose a theoretical description of the effect based on the first principles.

Published theories of the PB[4,5,6,7,8] use *ad hoc* rate equations for populations of spins and resonant phonons, considering the latter as a single dynamical variable. This is certainly an oversimplification, because the emitted phonons, having frequencies $\omega_{\mathbf{k}}$, form a group with a bell-like line shape with some width, centered around the spin transition frequency ω_0. For a single spin embedded into an infinite elastic matrix (as well as for a decaying atomic state in a free space) this line shape is Lorentzian with the width $\Gamma/2$, where Γ is the single-spin decay rate following from the Fermi golden rule.[9,10] However, in the case of many spins with a concentration sufficient to create a bottleneck, the line shape and line width of emitted phonons are unknown and should follow from the solution of the problem.

Van Vleck came to the idea of the phonon bottleneck comparing the rate of energy transfer from spins to phonons (obtained using experimental data) with the phonon relaxation rate $\Gamma_{\rm ph}$ due to different mechanisms and he found the latter to be typically too small to keep the phonon subsystem at equilibrium. However, the primary role in the PB problem belongs to another parameter that is not related to the phonon relaxation rate. This parameter is of a statistical origin and is defined as the ratio of the number of spins to the number of phonon modes within the single-spin line width Γ.[11] If this so-called bottleneck parameter B is vanishingly small, the spin excitation goes over into the phonon subsystem and never returns. In this case spins completely relax even without any phonon damping. However, for nonzero B and $\Gamma_{\rm ph} = 0$, the spin relaxation ends in the so-called bottleneck plateau that corresponds to a quasiequilibrium between spins and resonant phonons but not to the complete equilibrium. Further relaxation to the complete equilubrium can be achieved only if $\Gamma_{\rm ph}$ is taken into account. It should be stressed that the effective relaxation rate of the spins in this case is not $\Gamma_{\rm ph}$. It is much smaller and can be estimated as $\Gamma_{\rm ph}$ multiplied by the small fraction of phonon modes in the total number of modes (phonons + spins) involved in the process.

Although in many practical situations the number of resonant phonon modes is determined by the inhomogeneous broadening of spin levels, the pure spin-phonon model without inhomogeneous broadening has a fundamental importance. It was shown[11] that this model cannot be described *kinetically* (i.e., in terms of spin and phonon *populations* only) because of long-memory effects. In Ref. 11 memory effects have been taken into account within a minimal approximation, adding a new variable that can be interpreted as spin-phonon correlator. Analytical and numerical solutions of the resulting *reversible dynamical* equations show that the spin excitation approaches the botleneck plateau with damped oscillations. Inclusion of an *ad hoc* phonon damping $\Gamma_{\rm ph}$ into the bottleneck equations allows to describe the second stage of the relaxation towards the complete equilibrium.

Still, the solution of the PB problem in Ref. 11 is not completely satisfactory since it cannot produce a well-behaved line shape of emitted phonons. This indicates that additional nondiagonal correlators should be taken

into account that will make the description more complicated. Another important factor that should be taken into account is the inhomogeneous broadening of the spin levels.

This paper presents the exact numerical solution of the phonon bottleneck problem based on the Schrödinger equation for the spin-phonon system, with and without the *ad hoc* phonon damping and inhomogeneous spin broadening. The full Schrödinger equation for a many-body system is, of course, intractable by direct methods because of too many variables. However, the *low-excited* states of the system can be described by a *single excitation* that is hopping between spins and phonon modes. In this case the Hilbert space of the problem is severely truncated and one has to work with matrices the size of which is just the total number of spins and phonon modes under consideration. This is the case considered here and the solution of the PB problem is obtained by matrix algebra using Wolfram Mathematica. The results of the calculations show that for the pure model the spin excitation approaches the bottleneck plateau with oscillations, however, less revealed than in Ref. 11. The line width of emitted phonons broadens with the bottleneck parameter B.

The structure of the rest of the paper is the following. Sec. II sets up the Hamiltonian of the spin-phonon system and the Schrödinger equation (SE) in the case of a single excitation. The spin excitation and the initial conditions for problem are defined here. Sec. III presents the known results for the relaxation of a *single spin* and for the energy distribution of emitted phonons, used later for the reference. Sec. IV introduces the bottleneck parameter B for systems of many spins from statistical arguments, both with and without inhomogeneous spin broadening. Sec. V is the central section of the paper introducing the matrix formalism for the single-excitation spin-phonon problem. Here the expressions for the spin excitation $p(t)$, its asymptotic value p_∞ (the bottleneck plateau), and the asymptotic populations of the emitted phonons are obtained in terms of eigenvectors and eigenvalues of the dynamical matrix of the system. General analysis of the eigenstates of the dynamical matrix is done in Sec. VI. It is shown here that the number of the phonon modes "on speaking terms" with spins for the pure problem increases with B thus changing the statistical balance between spins and phonon modes. In this section the formulas describing the spectrum of the *split spin-phonon modes* and the hybridization of different phonon modes with each other (i.e., the scattering of phonons on spins) are obtained in terms of the eigenstates of the dynamical matrix. Sec. VII presents the results of numerical calculations for the pure model, including the split spin-phonon modes with the gap, time evolution of the spin excitation, bottleneck plateau, the post-plateau relaxation due to the phonon damping, and the energy distribution of the emitted phonons in the pure model. In Sec. VIII the effects of the inhomogeneous spin broadening are considered. The latter is shown to wash out oscillations of the spin excitation $p(t)$. Sec. IX contains the implementation of the general results to the spin relaxation between adjacent spin levels in molecular magnets. In Sec. X further problems of collective spin-phonons relaxation are discussed.

II. THE HAMILTONIAN AND SCHRÖDINGER EQUATION

Consider a spin-phonon Hamiltonian for N_S two-level systems (spins) put at positions $\mathbf{r}_i$ within an elastic body of N cells

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{1}$$

where

$$\hat{H}_0 = -\frac{1}{2}\sum_i \hbar\omega_{0i}\sigma_{iz} + \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}} \tag{2}$$

describes spins and harmonic phonons, $\boldsymbol{\sigma}$ being the Pauli matrix. The spin transition frequencies ω_i can differ from site to site. One can represent them in the form

$$\omega_{0i} = \overline{\omega_0} + \delta\omega_{0i}, \tag{3}$$

where $\delta\omega_{0i} \ll \overline{\omega_0}$ is the inhomogeneous broadening. In the absense of the latter we will simply use ω_0 as the spin transition frequency. Neglecting the processes that do not conserve the energy (that can be done in cases of practical significance where $\hat{V}$ can be treated as a perturbation), one can write $\hat{V}$ in the rotating-wave approximation (RWA) as

$$\hat{V} = -\frac{\hbar}{\sqrt{N}}\sum_i\sum_{\mathbf{k}}\left(A^*_{i\mathbf{k}} X^{01}_i a^\dagger_{\mathbf{k}} + A_{i\mathbf{k}} X^{10}_i a_{\mathbf{k}}\right), \tag{4}$$

where $A_{i\mathbf{k}} \equiv V_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}_i}$. In the numerical work below $V_{\mathbf{k}}$ will be replaced by a constant, $V_{\mathbf{k}} \Rightarrow V$. The operator $X^{10} \equiv \sigma_-$ brings the spin from the ground state $|\uparrow\rangle \equiv |0\rangle \equiv \binom{1}{0}$ to the excited state $|\downarrow\rangle \equiv |1\rangle \equiv \binom{0}{1}$ while $X^{01} \equiv \sigma_+$ does the opposite. Note that the state with no phonons and all spins in the ground state is the true ground state of the Hamiltonian above.

Below we will consider the low-excited states of the spin-phonon system that can be described by a superposition of the vacuum state of the system $|0\rangle$ (no phonons and all spins in the ground state) and the states with one excitation that is hopping between the spins and phonon modes. The wave function of these states has the form

$$\Psi = \left(c_0 + \sum_i c_i X^{10}_i + \sum_{\mathbf{k}} c_{\mathbf{k}} a^\dagger_{\mathbf{k}}\right)|0\rangle, \tag{5}$$

where the coefficients satisfy the system of equations

$$\frac{dc_0}{dt} = i\omega_0 c_0 \tag{6}$$

and

$$\begin{aligned}\frac{dc_i}{dt} &= -i\delta\omega_i c_i + \frac{i}{\sqrt{N}}\sum_{\mathbf{k}} A_{i\mathbf{k}} c_{\mathbf{k}} \\ \frac{dc_{\mathbf{k}}}{dt} &= -i\left(\omega_{\mathbf{k}} - \omega_0\right)c_{\mathbf{k}} + \frac{i}{\sqrt{N}}\sum_i A^*_{i\mathbf{k}} c_i,\end{aligned} \tag{7}$$

up to an irrelevant global phase factor. One can see that the ground-state coefficient c_0 is decoupled from the other coefficients since the RWA Hamiltonian conserves the excitation number

$$p(t) + \sum_{\mathbf{k}} n_{\mathbf{k}}(t) = \text{const}, \tag{8}$$

where

$$p = \sum_i |c_i|^2, \qquad n_{\mathbf{k}} = |c_{\mathbf{k}}|^2 \tag{9}$$

are the excitation number of the spin subsystem and populations of the phonon modes. One can also define transverse spin polarization components by

$$\begin{aligned} \langle \sigma_+ \rangle &= \left\langle X^{01} \right\rangle = c_0^* \sum_i c_i. \\ \langle \sigma_- \rangle &= \langle \sigma_+ \rangle^*, \qquad \langle \sigma_x \rangle = \mathrm{Re} \langle \sigma_+ \rangle, \end{aligned} \tag{10}$$

etc. The main part of the time dependence of $\langle \sigma_+ \rangle$ is $e^{-i\omega_0 t}$. The absolute value of the transverse spin component

$$\langle \sigma_\perp \rangle \equiv \sqrt{\langle \sigma_x \rangle^2 + \langle \sigma_y \rangle^2} = |\langle \sigma_+ \rangle| \tag{11}$$

does not have this oscillating factor. In many practical situations $\langle \sigma_\perp \rangle$ decays with time due to the inhomogeneous broadening. In the absence of the latter, the only source of the decoherence is interaction with phonons.

Our task is to find the time evolution $p(t)$ and $\langle \sigma_\perp \rangle_t$ starting from a particular initial state. In this work we restrict ourselves to the initial states with no phonons, $c_{\mathbf{k}}(0) = 0$. The simplest initial condition in this case is one spin at site i_0 excited and all other spins in their ground states:

$$c_{i_0}(0) = 1, \qquad c_{i \neq i_0}(0) = 0. \tag{12}$$

Another kind of the initial spin state is the state with the excitation equidistributed over all spins:

$$c_i(0) = e^{i\phi_i}/\sqrt{N_S}. \tag{13}$$

The initial spin state with random phases

$$\left\langle e^{i(\phi_i - \phi_j)} \right\rangle = \delta_{ij}, \tag{14}$$

is called incoherent. If ϕ_i are constant or they periodically change in space with some wave vector $\mathbf{q}_0$, the initial state is coherent. One can consider other kinds of spin initial conditions, say, excitation distributed over spins in some compact region of space.

III. NON-BOTTLENECKED SPIN-LATTICE RELAXATION

The results of this section can be found in the literature,[9,10] still a concise description of the non-bottlenecked spin-phonon dynamics is presented for the sake of consistency and future reference.

A. Relaxation of a single spin

Suppose there is a single spin, $c_i = c$, in the initially excited state. With a proper choice of the origin of the coordinate system one has $A_{i\mathbf{k}} = V_{\mathbf{k}}$. Using the Schrödinger equation (7), one can integrate the equations for the phonon modes $c_{\mathbf{k}}$:

$$\begin{aligned} c_{\mathbf{k}}(t) &= \frac{iV_{\mathbf{k}}^*}{\sqrt{N}} \int_{t_0}^{t} dt' e^{-i(\omega_{\mathbf{k}} - \omega_0)(t-t')} c(t') \\ &= \frac{iV_{\mathbf{k}}^*}{\sqrt{N}} \int_0^{t-t_0} d\tau e^{-i(\omega_{\mathbf{k}} - \omega_0)\tau} c(t-\tau) \end{aligned} \tag{15}$$

and insert the result into the equation for the spin c:

$$\frac{dc}{dt} = -\frac{1}{N} \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \int_0^{t-t_0} d\tau e^{-i(\omega_{\mathbf{k}} - \omega_0)\tau} c(t-\tau). \tag{16}$$

In this integro-differential equation, $c(t-\tau)$ is a slow function of time, whereas the memory function $f(\tau) = (1/N) \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 e^{-i(\omega_{\mathbf{k}} - \omega_0)\tau}$ is sharply peaked at $\tau = 0$. Thus one can replace $c(t-\tau) \Rightarrow c(t)$, after which integration over τ and keeping only real contribution responsible for the relaxation yields the equation

$$\frac{dc}{dt} = -\frac{\Gamma}{2} c, \tag{17}$$

where

$$\Gamma = \frac{2\pi}{N} \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \delta(\omega_{\mathbf{q}} - \omega_0) \tag{18}$$

is the single-spin decay rate. For $V_{\mathbf{k}} = V$ independently of the direction of $\mathbf{k}$, Γ can be written as

$$\Gamma = 2\pi |V|^2 \rho_{\mathrm{ph}}(\omega_0), \tag{19}$$

where

$$\rho_{\mathrm{ph}}(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \delta(\omega_{\mathbf{k}} - \omega) \tag{20}$$

is the phonon density of states normalized by one. The accuracy of the above short-memory approximation is justified by $\Gamma \ll \omega_0$. The δ-function in Eq. (18) implies that the spin is relaxing to a large number of phonon modes so that summation is replaced by integration,

$$\frac{1}{N} \sum_{\mathbf{k}} \ldots \Longrightarrow \int \frac{d^d k}{(2\pi)^d} \ldots, \tag{21}$$

where d is spatial dimension. In small bodies with essentially discrete phonon modes Eq. (21) is invalid. The solution of Eq. (17) with $t_0 = 0$ is $c(t) = e^{-(\Gamma/2)t}$ that leads to well-known decay rule for the spin excitation

$$p(t) = e^{-\Gamma t}. \tag{22}$$

The rate of transverse spin relaxation according to Eqs. (10) and (17) is $\Gamma/2$.

A similar elimination of phonons can be performed in the case of many spins in the absence of the PB.[12] The resulting equations describe collective spin-phonon relaxation, including superradiance.[3]

B. Distribution of emitted phonons

After the time dependence $c(t)$ has been found, one can return to Eq. (15) and calculate $c_{\mathbf{q}}(t)$. With $t_0 = 0$ the result is

$$c_{\mathbf{k}}(t) = \frac{iV_{\mathbf{k}}^*}{\sqrt{N}} \frac{e^{-i(\omega_{\mathbf{k}}-\omega_0)t} - e^{-\Gamma t/2}}{-i\left(\omega_{\mathbf{k}}-\omega_0\right)+\Gamma/2}. \tag{23}$$

This leads to the distribution of emitted phonons

$$n_{\mathbf{k}}(t) = |c_{\mathbf{k}}(t)|^2 = \frac{|V_{\mathbf{k}}|^2}{N} \frac{1-2e^{-\Gamma t/2}\cos\left[\left(\omega_{\mathbf{k}}-\omega_0\right)t\right]+e^{-\Gamma t}}{\left(\omega_{\mathbf{k}}-\omega_0\right)^2+\Gamma^2/4} \tag{24}$$

that asymptotically becomes the Lorentzian function

$$n_{\mathbf{k}} = \frac{1}{N} \frac{|V_{\mathbf{k}}|^2}{\left(\omega_{\mathbf{k}}-\omega_0\right)^2+\Gamma^2/4}. \tag{25}$$

With the help of Eqs. (22) and (24) one can check that the total excitation is conserved, in accordance with Eq. (8). For For $V_{\mathbf{k}} = V$ Eq. (25) can be rewritten as

$$n_{\mathbf{k}} = \frac{1}{\pi N \rho_{\mathrm{ph}}(\omega_0)} \frac{\Gamma/2}{\left(\omega_{\mathbf{k}}-\omega_0\right)^2+\Gamma^2/4}. \tag{26}$$

IV. THE PHONON BOTTLENECK

Let us now turn to systems with a macroscopic number of spins N_S. At least in the case of diluted spins, the relaxation is controlled by the bottleneck parameter B that can be defined as the ratio of the number of spins N_S to the number of phonon modes N_Γ within the natural spin line width Γ of Eq. (18),

$$N_\Gamma = \pi N \rho_{\mathrm{ph}}\left(\omega_0\right)\Gamma, \tag{27}$$

where $\rho_{\mathrm{ph}}\left(\omega\right)$ is given by Eq. (20). That is,[11]

$$B \equiv \frac{N_S}{N_\Gamma} = \frac{N_S}{\pi N \rho_{\mathrm{ph}}\left(\omega_0\right)\Gamma} = \frac{n_S}{\pi \rho_{\mathrm{ph}}\left(\omega_0\right)\Gamma}, \tag{28}$$

$n_S = N_S/N$ being the number of spins per unit cell. The definitions above pertain to a single phonon branch and extension to several phonon branches is obvious. For $B \lesssim 1$ (see below) N_Γ is the estimation of the number of phonon modes that can exchange excitation with spins.

In the case of a single spin, $N_S = 1$, in a macroscopic ($N \to \infty$) matrix the parameter B is vanishingly small. The excitation, initially localized at the spin, spreads with time over a large number N_Γ of resonant phonon modes, so that the spin relaxes completely according to Eq. (22). In simulations, the macroscopic limit is achieved if the average distance between the neighboring phonon modes becomes smaller than the natural line width Γ

$$\frac{1}{N\rho\left(\omega_0\right)} \ll \Gamma. \tag{29}$$

If the sample is so small that the spin can exchange excitation with only a few phonon modes, $N_\Gamma \sim 1$, it does not relax completely. In this case one has $B \sim 1$, the so-called phonon bottleneck situation. The simplest realization of the bottleneck is a system of two resonant states in which the excitation oscillates between the two states in time. If N_S is macroscopic but still $N_S \ll N_\Gamma$ and thus $B \ll 1$, the initial spin excitation is transferred irreversibly into the phonon subsystem, as is clear from statistical arguments. There is no bottleneck for $B \ll 1$, and the spin relaxation is still described by Eq. (22).

In the case of a finite concentration of spins n_S, the parameter B can easily become large. In this case only a small fraction of the excitation migrates into the phonon subsystem and the spins practically cannot relax as the emitted phonons are being absorbed by spins again. For $B \gg 1$, as we will immediately see, the number of the phonon modes "on speaking terms" with spins is not N_Γ but much greater. The latter can be obtained if one considers the spin-phonon hybridization. Inserting the spin Fourier components $b_{\mathbf{k}} \equiv \sum_i c_i e^{i\mathbf{k}\cdot\mathbf{r}_i}$ into the Schrödinger equation (7) and neglecting the coupling of modes with different values of $\mathbf{k}$, i.e., using $\sum_i \nu_i e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_i} \Rightarrow N_S\delta\left(\mathbf{k}-\mathbf{q}\right)$, one can reduce Eq. (7) to a 2×2 matrix problem that can be easily diagonalized. The eigenstates of this problem are hybridized spin-phonon modes with frequencies[13,14]

$$\Omega_{\mathbf{k}}^{(\pm)} = \frac{1}{2}\left\{\omega_{\mathbf{k}}-\omega_0 \pm \sqrt{\left(\omega_{\mathbf{k}}-\omega_0\right)^2+\Delta_{\mathbf{k}}^2}\right\}, \tag{30}$$

where

$$\Delta_{\mathbf{k}} = 2\sqrt{n_S}\,|V_{\mathbf{k}}| \tag{31}$$

is the spin-phonon splitting. These modes have the form of a straight line with a slope corresponding to phonons and a horizontal line corresponding to spins. The lines have an avoided level crossing at $\omega_{\mathbf{k}} = \omega_0$, split by $\Delta_{\mathbf{k}}$ that depends on the spin concentration. For $V_{\mathbf{k}} = V$ independently of the direction of $\mathbf{k}$, one can eliminate $\rho_{\mathrm{ph}}\left(\omega_0\right)$ from Eq. (28) with the help of Eqs. (20) and (18) and obtain the relation

$$B = \frac{2n_S\,|V|^2}{\Gamma^2} = \frac{\Delta^2}{2\Gamma^2}. \tag{32}$$

For $\Delta \gtrsim \Gamma$ the number of phonon modes strongly coupled to spins can be estimated as

$$N_\Delta = \pi N \rho_{\mathrm{ph}}\left(\omega_0\right)\frac{\Delta}{2}. \tag{33}$$

If n_S is so small that Δ falls below the natural spin line width Γ, one cannot speak of the hybridyzed spin-phonon modes. From Eq. (32) one obtains

$$N_\Delta = N_\Gamma\sqrt{B/2}. \tag{34}$$

The number of resonant phonons N_{res} that exchange excitation with the spins can be estimated in the whole range of B as

$$N_{\mathrm{res}} = \begin{cases} N_\Gamma, & B \lesssim 1 \\ N_\Delta, & B \gtrsim 1. \end{cases} \tag{35}$$

For any $B > 0$, the spin excitation $p(t)$ does not relax to zero but reaches a plateau at some p_∞ that from the statistical equidistribution argument can be estimated as

$$p_\infty = \frac{N_S}{N_S + N_{\rm res}} \tag{36}$$

with $N_{\rm res}$ defined above. We will see that this formula works well both for $B \lesssim 1$ and $B \gtrsim 1$, in the absence of the inhomogeneous broadening that will be considered in Sec. VIII. The asymptotes of the above expression are

$$p_\infty \cong \begin{cases} B, & B \ll 1 \\ 1 - 1/\sqrt{2B}, & B \gg 1, \end{cases} \tag{37}$$

in accordance with the numerical results of Sec. VII.

To describe the complete spin relaxation after the bottleneck plateau, one has to include the phonon relaxation processes, the easiest way being ascribing an empirical relaxation rate $\Gamma_{\rm ph}$ to the phonons.

V. DYNAMIC MATRIX AND THE TIME EVOLUTION OF THE SYSTEM

For the numerical solution of Eq. (7) it is convenient to introduce the state vector $\mathbf{C} = (\{c_i\}, \{c_{\mathbf{k}}\})$ and rewrite Eq. (7) in the form

$$\frac{d\mathbf{C}}{dt} = -i\mathbf{\Phi} \cdot \mathbf{C}, \tag{38}$$

where $\mathbf{\Phi}$ is the dynamical matrix of the spin-phonon system. In the absence of phonon damping, $\mathbf{\Phi}$ is Hermitean. Since the number of discreet phonon modes is N, $\mathbf{\Phi}$ is a $(N_S + N) \times (N_S + N)$ matrix. There are three methods of numerical solution of this equation that can be implemented in the Wolfram Mathematica.

The first method is the direct numerical solution using one of the ordinary-differential equations (ODE) solvers. This method is fast, can be made much faster if Mathematica is replaced by one of programming languages, it does not require high accuracy, but it does not allow to analytically average over the random phases in Eq. (13). This averaging can only be done if one runs the calculation many times with different realizations of initial conditions.

The second method is based upon numerical calculation of the matrix exponentials in the solution of Eq. (38) $\mathbf{C}(t) = e^{-i\mathbf{\Phi}t}\mathbf{C}(0)$. This method is slower than the direct ODE solution, it also does not require high accuracy, and here one can average over the initial conditions analytically.

The third method uses the expansion of the solution $\mathbf{C}(t)$ over eigenvectors of $\mathbf{\Phi}$. This method allows analytical averaging over initial conditions, it is faster than the method using matrix exponentials, if formulated in a fully vectorized form. However, this method requires high precision and for large matrices it runs on 64-bit machines only. Note that arbitrary-precision computations on 32-bit machines with Mathematica are possible but they are very slow. An important advantage of this method is that it allows to obtain formulas for the asymptotic $t \to \infty$ state of the system in terms of matrices.

Below, the method based on the eigenvectors of $\mathbf{\Phi}$ will be used. In the general case when the *ad hoc* phonon damping $\Gamma_{\rm ph}$ is added, $\mathbf{\Phi}$ is non-Hermitean, and one has to distinguish between right and left eigenvectors. The dynamical matrix $\mathbf{\Phi}$ has $N_S + N$ right eigenvectors $\mathbf{R}_\mu$ that satisfy

$$\mathbf{\Phi} \cdot \mathbf{R}_\mu = (\Omega_\mu - i\Gamma_\mu)\, \mathbf{R}_\mu. \tag{39}$$

In the eigenvalues, the imaginary parts Γ_μ originate from $\Gamma_{\rm ph}$. The size of the matrix $\mathbf{\Phi}$ can be reduced if the phonon modes far from the resonance are dropped. The solution of Eq. (38) can be expanded over the complete orthonormal set of $\mathbf{R}_\mu$ as follows

$$\mathbf{C}(t) = \sum_\mu \mathbf{R}_\mu e^{-(i\Omega_\mu + \Gamma_\mu)t} \mathbf{L}_\mu \cdot \mathbf{C}(0), \tag{40}$$

where $\mathbf{L}_\mu$ are left eigenvectors of $\mathbf{\Phi}$ that satisfy $\mathbf{L}_\mu \cdot \mathbf{R}_\nu = \delta_{\mu\nu}$. Note that, in general, $\mathbf{R}_\mu$ and $\mathbf{L}_\mu$ are not complex conjugate. The vectorized form of Eq. (40) is

$$\mathbf{C}(t) = \mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} \cdot \mathbf{C}(0), \tag{41}$$

where $\mathbf{E}$ is the right-eigenvector matrix composed of all eigenvectors $\mathbf{R}_\mu$ standing vertically, $\mathbf{E}^{-1}$ is left-eigenvector matrix, composed of all left eigenvectors lying horizontally, and $\mathbf{W}(t)$ is the diagonal matrix with the elements $e^{-(i\Omega_\mu + \Gamma_\mu)t}$. In fact, $\mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} = e^{-i\mathbf{\Phi}t}$.

A. Longitudinal relaxation of spins

Now the spin excitation $p(t)$ can be written with the help of Eqs. (9) and (41) in the vectorized form

$$p(t) = \left(\mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} \cdot \mathbf{C}(0)\right)_S \cdot (\text{h.c.})_S\,, \tag{42}$$

where the subscript S means projection onto the spin subspace. Eq. (42) can be used for a fast computation. For the incoherent initial condition, Eqs. (13) and (14), one obtains

$$p(t) = \frac{1}{N_S} \mathrm{Tr}_S \left[\left(\mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1}\right)_S \cdot (\text{h.c.})_S\right], \tag{43}$$

where the trace is taken over spin indices only. A more explicit form of Eq. (42) is

$$\begin{aligned} p(t) \;=\; & \sum_{\mu\nu} e^{-(\Gamma_\mu + \Gamma_\nu)t} \cos\left[(\Omega_\mu - \Omega_\nu)\, t\right] \sum_{n=1}^{N_S} R^*_{\mu n} R_{\nu n} \\ & \times \sum_{n'=1}^{N_S} L_{\nu n'} C_{n'}(0) \sum_{n''=1}^{N_S} L^*_{\mu n''} C^*_{n''}(0). \end{aligned} \tag{44}$$

In the absence of phonon damping, $\Gamma_\mu = 0$, there is a nonzero asymptotic value of p that can be obtained from the equation above by dropping all oscillating terms, i.e.,

setting $\mu = \nu$. This corresponds to the diagonal density matrix of the spin-phonon system. Taking into account $L^*_{\mu n} = R_{\mu n}$ in the Hermitean case, one obtains

$$p_\infty = \sum_\mu \sum_{n=1}^{N_S} |R_{\mu n}|^2 \left| \sum_{n'=1}^{N_S} R^*_{\mu n'} C_{n'}(0) \right|^2 . \qquad (45)$$

For the incoherent initial condition this simplifies to

$$p_\infty = \frac{1}{N_S} \sum_\mu \left(\sum_{n=1}^{N_S} |R_{\mu n}|^2 \right)^2 . \qquad (46)$$

Note that in the macroscopic limit $N \to \infty$ for a single spin Eq. (44) should assume the simple exponential form of Eq. (22) and $p_\infty = 0$. The same should be the case for any finite N_S.

If the phonon damping $\Gamma_{\rm ph}$ is finite but small, the process of spin relaxation is two-stage. First, the spin subsystem equilibrates with the subsystem of resonant phonons and $p(t)$ is mainly changing due to the time dependence of the terms with $\mu \neq \nu$ in Eq. (44), whereas the role of Γ_μ is insignificant. At the end of this stage the terms with $\mu \neq \nu$ die out, and the further slow relaxation is governed by Γ_μ. In particular, for the incoherent initial condition Eq. (44) at the second stage of the relaxation becomes

$$p(t) = \frac{1}{N_S} \sum_\mu e^{-2\Gamma_\mu t} \sum_{n=1}^{N_S} |R_{\mu n}|^2 \sum_{n'=1}^{N_S} |L_{\mu n'}|^2 . \qquad (47)$$

Since for macroscopic systems the number of different values of Γ_μ in this expression is very large, the dependence $p(t)$ is a combination of many different exponentials, i. e., $p(t)$ is nonexponential.

In the limit we study in the paper, $k_0 r_0 \gg 1$, the solution $p(t)$ is actually the same for coherent and incoherent initial conditions. The only difference is that for the incoherent initial condition averaging over the initial phases of spins leads to reproducible results for different realizations of the nondiagional elements of $\mathbf{\Phi}$. For coherent initial conditions, one obtains somewhat different results for different realizations of the spin-phonon matrix elements, related to location of the individual spins in space. These differences persist with increasing the number of spins and phonon modes, so that there is no self-avereaging. The computation of $p(t)$ in the coherent case is faster but averaging over spin configurations is needed.

B. Transverse relaxation of spins

Let us now consider the time evolution of the transverse spin polarization given by Eq. (11) starting from the fully coherent initial condition

$$c_i = \frac{\sin\theta}{\sqrt{N_S}}, \qquad c_0 = \cos\theta \qquad (48)$$

that satisfies the normalization condition $|c_0|^2 + \sum_i |c_i|^2 = 1$ for the wave function of Eq. (5) in the case of initial phonon vacuum. In Eq. (48) θ is the angle between the spin vector and the z-axis. In the initial state one has

$$\langle \sigma_\perp \rangle_0 = \sqrt{N_S} \sin\theta \cos\theta \qquad (49)$$

that can be used to define the normalized transverse spin polarization

$$f_\perp(t) = \langle \sigma_\perp \rangle_t \,/\, \langle \sigma_\perp \rangle_0 \qquad (50)$$

that satisfies $f_\perp(0) = 1$. With the help of Eq. (41) one obtains the vectorized expression

$$f_\perp(t) = \left| \frac{1}{N_S} \sum_{nn'=1}^{N_S} \left(\mathbf{E} \cdot \mathbf{W}(t) \cdot \mathbf{E}^{-1} \right)_{nn'} \right| . \qquad (51)$$

Note that this formula is explicitly independent of the angle θ. An alternative expression for $f_\perp(t)$ following from Eq. (40) has the form

$$f_\perp(t) = \left| \sum_\mu T_\mu e^{-(i\Omega_\mu + \Gamma_\mu)t} \right| , \qquad (52)$$

where

$$T_\mu \equiv \frac{1}{N_S} \sum_{n=1}^{N_S} R_{\mu n} \sum_{n'=1}^{N_S} L_{\mu n'} . \qquad (53)$$

In the case of undamped phonons one has $L^*_{\mu n} = R_{\mu n}$ and $T_\mu = (1/N_S) \left| \sum_{n=1}^{N_S} R_{\mu n} \right|^2$ is real. Then, dropping oscillating terms in Eq. (52) at large times one obtains the asymptotic value $f_\perp(\infty) = \sqrt{\sum_\mu |T_\mu|^2}$ [c.f. transition from Eq. (44) to Eq. (45)]. It can be easily shown that in the presence of inhomogeneous broadening and in the absence of the coupling to phonons $f_\perp(\infty) \to 0$ in the thermodynamic limit. The same should hold in the presence of both inhomogeneous broadening and spin-phonon interaction since the former should be sufficient to cause complete decoherence. Analysis of the principally important case without the inhomogeneous broadening should be postponed until obtaining numerical results. For a single spin, coupling to phonons causes decoherence with the rate $\Gamma/2$, as was stressed at the end of Sec. (III A). In the case of the phonon bottleneck this decoherence should be slowed down since a few phonon modes couple to many spins, still the expected result is $f_\perp(\infty) = 0$.

C. Energy distribution of emitted phonons

The method formulated above can be used to find the state of the phonon system resulting from spin-phonon relaxation. Obviously it can be done for undamped phonons only. In the case of many spins there are no analytical results for the occupation numbers of emitted

phonons $n_{\mathbf{k}}$. in the literature. However, one can express $n_{\mathbf{k}}$ through the eigenstates of the dynamical matrix $\mathbf{\Phi}$ defined by Eqs. (38) and (39). For the wave function given by Eq. (5) one has $n_{\mathbf{k}} = |c_{\mathbf{k}}|^2$. Labeling the phonon modes by the discrete index l, one can express $n_{\mathbf{k}} \equiv n_l$ through the state vector $\mathbf{C}$ given by Eq. (40). For the incoherent initial spin state with the help of Eq. (14) one obtains, asymptotically,

$$n_l(\infty) = \frac{1}{N_S} \sum_{\mu} \sum_{n=1}^{N_S} |R_{\mu n}|^2 |R_{\mu, N_S+l}|^2 . \qquad (54)$$

For $N_S = 1$ this expression should reproduce Eq. (25).

VI. ANALYSIS OF THE EIGENSTATES OF THE SPIN-PHONON SYSTEM

A. Spinness and off-resonance phonon emission

Although the formalism of the preceding section is sufficient to describe the dynamics of the spin-phonon system in terms of transition between different bare (unperturbed) modes, it is also interesting to look closer at the true spin-phonon eigenstates. Throughout this section we consider phonons as undamped, $L^*_{\mu n} = R_{\mu n}$. The eigenstates are superpositions of spin and phonon states, so the first question would be to determine the fractions of spin and phonon states in any eigenstate, or, as it can be termed, their "spinness" and "phononness". For instance, the spinness of the state μ is defined by

$$Spinness_{\mu} = \sum_{n=1}^{N_S} |R_{\mu n}|^2 , \qquad (55)$$

while the phononness is defined by a similar expression with summation over phonon indices. Note that spinness enters the expression for the asymptotic spin excitation p_{∞}, Eq. (46). Obviously the sum of spinness and phononness of any state μ is 1. Spinness summed over μ gives the total number of spins. Far from the resonance the eigenstates are mainly phonon states, so that their spinness is small and can be calculated perturbatively. Labeling these states by the wave vector $\mathbf{k}$ instead of μ, one has $R_{\mathbf{qk}} \cong \delta_{\mathbf{qk}}$, where δ is the Kronecker symbol, and, in the first order of the perturbation theory,

$$R_{\mathbf{k}i} \cong -\frac{1}{\sqrt{N}} \frac{A_{i\mathbf{k}}}{\omega_{\mathbf{k}} - \omega_0}. \qquad (56)$$

With this one obtains

$$Spinness_{\mathbf{k}} \cong \frac{n_S |V_{\mathbf{k}}|^2}{(\omega_{\mathbf{k}} - \omega_0)^2} \Longrightarrow \frac{B}{2} \frac{\Gamma^2}{(\omega_{\mathbf{k}} - \omega_0)^2}. \qquad (57)$$

The last expression was obtained for $|V_{\mathbf{k}}|^2 = |V|^2$ with the help of Eq. (32). One can see that for a large bottleneck parameter the interaction of phonons with spins becomes large, so that phonon modes are noticeably distorted even relatively far from the resonance. This means, dynamically, that the number of phonon modes that exchange excitation with spins is not just a fixed number N_Γ determined by the single-spin relaxation rate Γ [see Eq. (27)] and it increases with B. Of course, Eq. (57) becomes inapplicable near the resonance. However, one can figure out its behavior for $B \gg 1$. In this case the spinness of the states near the resonance should approach 1. One can reproduce this behavior by adding $(B/2)\,\Gamma^2$ in the denominator of Eq. (57). This is in accordance with Eqs. (34) and (35) that define the number of phonon modes on speakng terms with the spins.

For $B \ll 1$ we will see that the spinness remains small everywhere including the resonance. This means that initially prepared states with the excitation localized on spins will decompose over the true eigenstates that have a very small fraction of spin states, so that the excitation will migrate completely into the phonon subsystem. To the contrary, for $B \gg 1$ the initially prepared state will decompose over eigenstates that have spinness close to 1, so that the excitation mostly remains on spins that is the phonon bottleneck.

Using Eqs. (56) and (54) allows one to obtain the probability of emission of a phonon with a wave vector $\mathbf{k}$ far from the resonance. With $\mu \Rightarrow \mathbf{q}$ one obtains

$$\begin{aligned} n_{\mathbf{k}} &= \frac{1}{N_S} \sum_{\mathbf{q}} \sum_{i=1}^{N_S} |R_{\mathbf{q}i}|^2 |R_{\mathbf{qk}}|^2 \\ &\cong \frac{1}{N_S} \sum_{i=1}^{N_S} |R_{\mathbf{k}i}|^2 = \frac{1}{N} \frac{|V_{\mathbf{k}}|^2}{(\omega_{\mathbf{k}} - \omega_0)^2}, \end{aligned} \qquad (58)$$

independently of the bottleneck parameter B. This result is in accord with Eq. (25).

B. Spin-phonon hybridization

To quantify the spin-phonon hybridization in the general case, one can introduce the average phonon detuning from the spins $\omega_{\mathbf{k}} - \omega_0$ in any eigenstate μ as

$$\langle \omega_{\mathbf{k}} - \omega_0 \rangle_{\mu} \equiv \frac{\sum_{\mathbf{k}} |R_{\mu\mathbf{k}}|^2 (\omega_{\mathbf{k}} - \omega_0)}{\sum_{\mathbf{k}} |R_{\mu\mathbf{k}}|^2}, \qquad (59)$$

where the denominator is the phononness of the eigenstate μ introduced above. Note that this definition does not include the momentum carried by spins. Thus Eq. (59) principally cannot completely reproduce the results for dense magnetic systems. Plotting $\langle \omega_{\mathbf{k}} - \omega_0 \rangle_{\mu}$ vs the energy (frequency) eigenvalues Ω_μ reveals that near the resonance there are pairs of the same detunings $\langle \omega_{\mathbf{k}} - \omega_0 \rangle_{\mu}$ for two different frequencies Ω_μ. In other words, the frequencies corresponding to the same $\langle \omega_{\mathbf{k}} - \omega_0 \rangle_{\mu}$ are split because of the spin-phonon interaction. Far from the resonance the relation between $\langle \omega_{\mathbf{k}} - \omega_0 \rangle_{\mu}$ and the frequency Ω_μ corresponds to a pure phonon mode.

C. Resonance scattering of phonons

One also can study the admixture of other phonon modes to the given phonon mode because of the phonon scattering on spins. This can be described by the dispersion

$$\delta\left\{\omega_{\mathbf{k}}-\omega_0\right\}_\mu \equiv \sqrt{\frac{\sum_{\mathbf{k}}\left|R_{\mu\mathbf{k}}\right|^2\left(\omega_{\mathbf{k}}-\omega_0-\left\langle\omega_{\mathbf{k}}-\omega_0\right\rangle_\mu\right)^2}{\sum_{\mathbf{k}}\left|R_{\mu\mathbf{k}}\right|^2}}. \tag{60}$$

Far from the resonance the eigenstates are almost pure phonons, so that $\delta\left\{\omega_{\mathbf{k}}-\omega_0\right\}_\mu$ is small. At resonance $\delta\left\{\omega_{\mathbf{k}}-\omega_0\right\}_\mu$ has a maximum that corresponds to the resonance scattering.

VII. NUMERICAL RESULTS AND ANALYSIS

This section has been omitted to reduce the size. Please, get the full text of the paper here:

www.lehman.edu/faculty/dgaranin/Bottleneck2.pdf

VIII. INHOMOGENEOUS BROADENING OF SPIN LEVELS

In some systems the inhomogeneous broadening defined by Eq. (3) is much larger than the natural spin linewidth Γ or the spin-phonon splitting Δ. The number of spins within the frequency interval $d\omega_0$ around the frequency ω_0 is

$$dN_S = N_S\rho_S(\omega_0)d\omega_0, \tag{61}$$

where the spin density of states $\rho_S(\omega_0)$ satisfies $\int_0^\infty \rho_S(\omega_0)d\omega_0 = 1$. An example is the Gaussian line shape

$$\rho_S(\omega_0) = \frac{1}{\sqrt{2\pi}\delta\omega_0}\exp\left[-\frac{\left(\omega_0-\overline{\omega_0}\right)^2}{2\left(\delta\omega_0\right)^2}\right]. \tag{62}$$

In the presence of a large inhomogeneous broadening the number of phonons on speaking terms with spins can be estimated as $N_{\delta\omega_0}\sim N\pi\rho_{\rm ph}(\omega_0)\delta\omega_0$ that should replace N_Γ of Eq. (27) in the definition of the bottleneck parameter B that becomes smaller than for the pure model by a factor of $\delta\omega_0/\Gamma \gg 1$. Consideration of this kind can be found in Van Vleck's original paper[2] and subsequent publications. In fact, as we shall see below in this section, the relation between the numbers of spins and phonon modes that can exchange excitation is different in different frequency regions within the inhomogeneous spin line width $\delta\omega_0$ and a frequency-resolved description of the phonon bottleneck is possible.

In simulations the macroscopic limit is achieved if the average distance between the neigboring spin levels becomes smaller than the natural line width Γ

$$\frac{1}{N_S\rho_S(\omega_0)} \ll \Gamma, \tag{63}$$

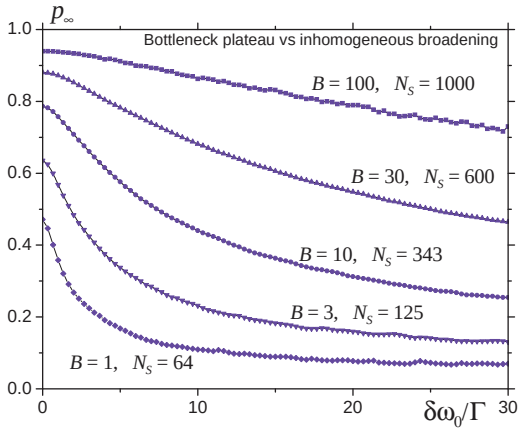

FIG. 1: The bottleneck plateau in the case of inhomogeneous broadening with the Gaussian line shape vs $\delta\omega_0$.

c.f. Eq. (29). Since both of these conditions should be satisfied, both N and N_S should be large enough. The results for the bottleneck plateau p_∞ vs the inhomogeneous broadening $\delta\omega_0$ in Eq. (62), obtained numerically from Eq. (46) are shown in Fig. 1. Since the number of phonons that can exchange energy with spins increases with $\delta\omega_0$, the bottleneck plateau p_∞ decreases. For $B \lesssim 1$, the most pronounced decrease occurs at $\delta\omega_0 \sim \Gamma$, the crossover from the natural line width to the inhomogeneous line width. In the case $B \gg 1$ this crossover occurs at $\delta\omega_0 \sim \sqrt{B}\Gamma \sim \Delta$, in accordance with the comments after Eq. (57).

Clearly for $\delta\omega_0 \gg \Gamma, \Delta$ much more phonons can exchange their energy with spins, so that the bottleneck condition is alleviated and spin relaxation is facilitated. In this case the problem simplifies since spins and phonons exchange energy only within the frequency interval of order $\max(\Gamma,\Delta)$ that is much narrower than the inhomogeneous line width $\delta\omega_0$. Thus one can split the latter into the frequency intervals $\Delta\omega_0$ around ω_0 that satisfy $\max(\Gamma,\Delta) \ll \Delta\omega_0 \ll \delta\omega_0$ and consider the energy exchange between spins and phonons in each of these intervals independently. The spin and phonon densities of states within each interval $\Delta\omega_0$ can be considered as constants and they define the bottleneck parameter in a frequency interval around ω_0

$$B_{\omega_0} \equiv \frac{N_S}{N}\frac{\rho_S(\omega_0)}{\rho_{\rm ph}\left(\omega_0\right)} = n_S\frac{\rho_S(\omega_0)}{\rho_{\rm ph}\left(\omega_0\right)}. \tag{64}$$

Since the phonon density of states is a smooth function, one can replace $\rho\left(\omega_0\right) \Rightarrow \rho\left(\overline{\omega_0}\right)$. On the other hand, $\rho_S(\omega_0)$ and thus B_{ω_0} have a maximum at $\omega_0 = \overline{\omega_0}$. One can parametrize

$$B_{\omega_0} = \frac{\rho_S(\omega_0)}{\rho_S(\overline{\omega_0})}B_{\overline{\omega_0}}, \tag{65}$$

where $B_{\overline{\omega_0}}$ is the bottleneck parameter at the center of the line. For a Gaussian line shape of Eq. (62) one has

$$B_{\overline{\omega_0}} = \frac{n_S}{\sqrt{2\pi}\rho_{\rm ph}\left(\omega_0\right)\delta\omega_0}. \tag{66}$$

The spin excitation reaches a frequency-dependent plateau $p_\infty(\omega_0)$ that depends on B_{ω_0}. The average over the spin line shape $\rho_S(\omega_0)$ of Eq. (61) now becomes

$$\overline{p_\infty} = \int_0^\infty d\omega_0 \rho_S(\omega_0) p_\infty(\omega_0). \tag{67}$$

Evidently $\overline{p_\infty} < p_\infty(\overline{\omega_0})$ since the bottleneck effect weakens away from the center of the spin band. The numerically found dependence of $p_\infty(\omega_0)$ is very close to

$$p_\infty(\omega_0) = \frac{B_{\omega_0}}{1 + B_{\omega_0}} \tag{68}$$

that can be expected from general statistical arguments. This important formula will be used below to obtain results for the bottleneck plateau taking into account the inhomogeneously broadened spin line shape. The illustrations will be done for the Gaussian line shape of Eq. (62).

In the case $B_{\overline{\omega_0}} \ll 1$ one obtains

$$\overline{p_\infty} \cong B_{\overline{\omega_0}} \int_0^\infty d\omega_0 \frac{[\rho_S(\omega_0)]^2}{\rho_S(\overline{\omega_0})} \tag{69}$$

that with the help of Eq. (62) yields

$$\overline{p_\infty} \cong B_{\overline{\omega_0}}/\sqrt{2}. \tag{70}$$

If $B_{\overline{\omega_0}} \gg 1$, one can use

$$\overline{p_\infty} = 1 - \int_0^\infty d\omega_0 \frac{\rho_S(\omega_0)}{1 + B_{\omega_0}} \tag{71}$$

that follows from Eq. (68). The integrand of this expression is close to $\rho_S(\overline{\omega_0})/B_{\overline{\omega_0}} = \text{const}$ for $B_{\omega_0} \gtrsim 1$ and it decays abruptly further from the center of the spin line where $B_{\omega_0} \lesssim 1$. Let us define ω^* that satisfies $B_{\omega^*} = 1$, that is, $\rho_S(\omega^*) = \rho_S(\overline{\omega_0})/B_{\overline{\omega_0}}$. Then from Eq. (71) one obtains, approximately,

$$\overline{p_\infty} \cong 1 - \frac{2\delta\omega^* \rho_S(\overline{\omega_0})}{B_{\overline{\omega_0}}}, \tag{72}$$

where $\delta\omega^* \equiv |\omega^* - \overline{\omega_0}|$. For the Gaussian line shape of Eq. (62) one has $\delta\omega^* = \delta\omega_0\sqrt{2\ln B_{\overline{\omega_0}}}$ and, finally,

$$\overline{p_\infty} \cong 1 - \frac{2}{B_{\overline{\omega_0}}}\sqrt{\frac{\ln B_{\overline{\omega_0}}}{\pi}}, \qquad B_{\overline{\omega_0}} \gg 1. \tag{73}$$

Fig. 2 shows $\overline{p_\infty}$ in the whole interval of $B_{\overline{\omega_0}}$ calculated numerically from Eqs. (62), (67), and (65).

Next we calculated the time dependence of the spin excitation $p(t)$ for spins within a frequency interval $\Delta\omega_0$ around ω_0 that satisfies $\max(\Gamma, \Delta) \ll \Delta\omega_0 \ll \delta\omega_0$, as explained above. Again, the incoherent initial condition for spins leading to Eq. (46) was used. Only spins and phonon modes within the interval $\Delta\omega_0$ were taken into account while all other spins and phonon modes have been ignored. This allowed to greatly reduce the computation time. The results have been shown to be

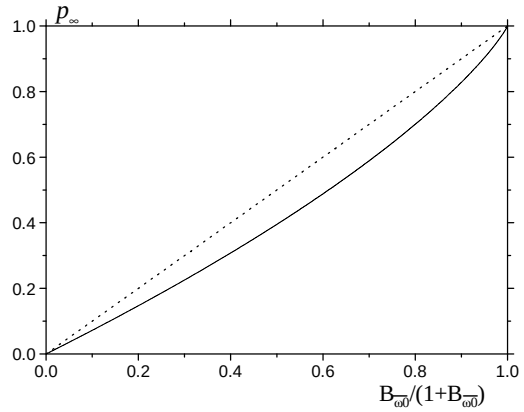

FIG. 2: The bottleneck plateau in the case of strong ($\delta\omega_0 \gg \Gamma, \Delta$) inhomogeneous broadening with the Gaussian line shape vs the bottleneck parameter B_{ω_0}.

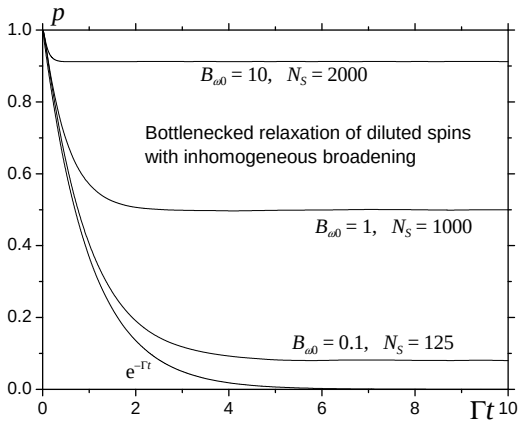

FIG. 3: Time dependence of the spin excitation $p(t)$ for the spins with frequencies around ω_0 in the case of strong inhomogeneous broadening.

practically independent of $\Delta\omega_0$ as soon as the condition $\Gamma \ll \Delta\omega_0$ is fullfilled. The distribution of spin frequencies within $\Delta\omega_0$ was taken equidistant (similarly to the phonon modes) that allowed to eleminate statistical scattering. In this realization of the model, spins and phonon modes form two equivalent groups interacting with each other. The results of computations for undamped phonons are shown in Fig. 3. Note that here oscillations visible in Fig. **??** are completely washed out. The asymptotic values of p are in accord with Eq. (68). Having the results for $p(t)$ for any ω_0, one could perform now integration over spin frequencies ω_0 similarly to Eq. (67) using, e.g., Eq. (62).

One can compare the results of the present calculation within the frequency interval $\Delta\omega_0$ with the results of the earlier general calculation shown in Fig. 1. The connection is provided by the identity

$$B_{\overline{\omega_0}} = \sqrt{\frac{\pi}{2}}\frac{\Gamma}{\delta\omega_0} B \tag{74}$$

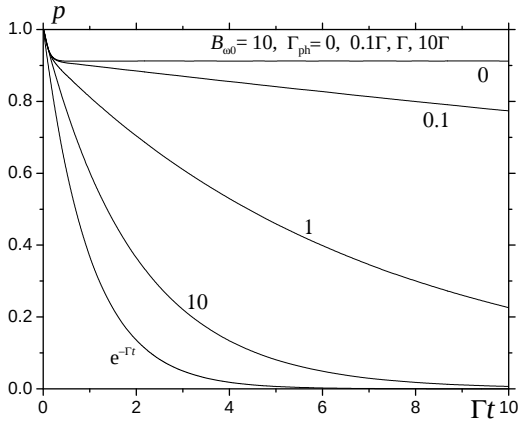

FIG. 4: The same in the case of damped phonons. Again, for $B \gg 1$ the effective spin relaxation rate is much smaller than the phonon relaxation rate $\Gamma_{\rm ph}$.

that follows from Eqs. (28), (64), and (62). For instance, the rightmost point of the curve $B = 1$ in Fig. 1 is $p_\infty \simeq 0.070$ for $\delta\omega_0/\Gamma = 30$. Eq. (74) yields then $B_{\overline{\omega_0}} \simeq 0.0418$. For such small $B_{\overline{\omega_0}}$ one can use Eq. (70) that yields $p_\infty \simeq 0.030$. The disagreement with the value $p_\infty \simeq 0.070$ can be explained by the fact that the number of spins $N_S = 64$ in the general calculation for $B = 1$ is too small to reach the asymptotic result given by Eq. (68) and statistical scattering is still substantial. For the rightmost point of the curve $B = 3$ in Fig. 1 the disagreement between the results of the two calculations is smaller.

The results for spin relaxation in the case of damped phonons are shown in Fig. 4. One can see that for $B \gg 1$ the effective spin relaxation rate is much smaller than the phonon relaxation rate $\Gamma_{\rm ph}$, similarly to the case without inhomogeneous broadening, see Fig. **??**.

IX. IMPLEMENTATION FOR MOLECULAR MAGNETS

Let us work out the general expressions and estimate the parameters that govern the bottlenecked spin relaxation for molecular magnets, in particular, for the most popular compound Mn_{12}. Historically, the phonon botteneck was first observed in other systems. However, there is an experimental evidence of the phonon bottleneck in molecular magnets as well. On the other hand, molecular magnets are especially convenient because of the universal form of the spin-phonon relaxation that does not depend on any unknown spin-phonon coupling constants.[15] The spin relaxation between the adjacent levels of the uniaxial spin Hamiltonian $-DS_z^2$ is due to the rotation of the crystallographic easy axis by the transverse phonons. The rate of decay from the first excited state $|-S+1\rangle$ to the ground state $|-S\rangle$ is given by the formula

$$\Gamma = \frac{S(2S-1)^2 D^2 \omega_0^3}{12\pi\hbar\rho v_t^5}, \qquad (75)$$

where ρ is the mass density and v_t is the speed of the transverse phonons. The most recent derivation of this formula for the transitions between any adjacent spin levels can be found in Appendix A of Ref. 16. In zero field one has $\hbar\omega_0 = E_{-S+1} - E_{-S} = (2S-1)D$ and Eq. (75) can be cast into the elegant form

$$\Gamma = \frac{S}{12\pi}\frac{\omega_0^5}{\Omega_t^4}, \qquad \Omega_t \equiv \left(\frac{\rho v_t^5}{\hbar}\right)^{1/4}. \qquad (76)$$

The phonon density of states of Eq. (20), multiplied by the number 2 of transverse phonon modes, has the form

$$\rho_{\rm ph}(\omega_0) = \frac{1}{\pi^2}\frac{\omega_0^2}{\widetilde{\Omega}_D^3}, \qquad \widetilde{\Omega}_D \equiv \frac{v_t}{v_0^{1/3}}, \qquad (77)$$

where v_0 is the unit-cell volume. The frequency $\widetilde{\Omega}_D$ is related to the Debye frequency Ω_D as $\Omega_D = (6\pi^2)^{1/3}\widetilde{\Omega}_D$. Thus the bottleneck parameter B of Eq. (28) becomes

$$B = \frac{12\pi^2}{S}\frac{\Omega_t^4\widetilde{\Omega}_D^3}{\omega_0^7} n_S. \qquad (78)$$

For Mn_{12} one has $S = 10$, $\rho = 1.83$ g/cm^3, $v_0 = 3716$ Å^3, and from the heat-capacity measurements[17] follows $\hbar\Omega_D/k_B \simeq 38$ K thus $\hbar\widetilde{\Omega}_D/k_B \simeq 10$ K. Further one obtains $v_t \simeq 2\times 10^3$ m/s and $\hbar\Omega_t/k_B \simeq 210$ K, whereas $\hbar\omega_0/k_B \simeq 12$ K. Plugging these parameters into Eq. (78) one obtains $B \simeq 5\times 10^5 n_S$. This means that for a non-diluted Mn_{12} crystal, $n_S = 1$, the bottleneck parameter is huge.

Of course, for non-diluted magnetic crystals the physics includes the effects of coherence and it is more complicated than just the phonon bottleneck. The pure bottleneck situation is realized for a sufficient dilution, so that $k_0 r_0 \gtrsim 2\pi$ and the phases of emitted and reabsorbed phonons can be considered as random. Using $r_0 = (v_0/n_S)^{1/3}$ for the average distance between the neighboring magnetic molecules and $k_0 = \omega_0/v_t$, one can rewrite the condition of sufficient dilution as

$$n_S \lesssim n_S^* \equiv \left(\frac{\omega_0}{2\pi\widetilde{\Omega}_D}\right)^3. \qquad (79)$$

We call n_S^* critical concentration or critical dilution. With the parameters above, one obtains $n_S^* \simeq 0.008$. Even at this dilution, the bottleneck parameter remains huge,

$$B^* \equiv \frac{12\pi^2}{S}\frac{\Omega_t^4\widetilde{\Omega}_D^3}{\omega_0^7} n_S^* = \frac{3}{2\pi S}\left(\frac{\Omega_t}{\omega_0}\right)^4 \qquad (80)$$

that numerically yields $B^* \simeq 4000$. Note that for spin transitions between excited levels the energy differences $\hbar\omega_0 = E_{m+1} - E_m = -(2m+1)D$ are smaller than above, thus the values of B are even larger.

Now from Eq. (19) one obtains the estimation of the spin-phonon matrix element

$$|V|^2 = \frac{\Gamma}{2\pi\rho_{\rm ph}(\omega_0)} = \frac{S}{24}\frac{\omega_0^3\widetilde{\Omega}_D^3}{\Omega_t^4}. \qquad (81)$$

(that also could be obtained directly!). This yields the spin-phonon splitting of Eq. (31) in the form

$$\Delta = \sqrt{n_S}\sqrt{\frac{S}{6}\frac{\omega_0^3\widetilde{\Omega}_D^3}{\Omega_t^4}} \tag{82}$$

and

$$\Delta^* = \sqrt{n_S^*}\sqrt{\frac{S}{6}\frac{\omega_0^3\widetilde{\Omega}_D^3}{\Omega_t^4}} = \sqrt{\frac{S}{6}}\frac{1}{(2\pi)^{3/2}}\frac{\omega_0^3}{\Omega_t^2}. \tag{83}$$

Numerically one obtains $\hbar\Delta/k_B \simeq 40\sqrt{n_S}$ mK and $\hbar\Delta^*/k_B \simeq 3.6$ mK.

Let us now discuss the role of inhomogeneous broadening on the phonon bottleneck in molecular magnets. First, there is the dipole-dipole interaction (DDI) that is as strong as about $E_{DDI}/k_B \simeq 67$ mK between the two neighboring Mn_{12} molecules. This would result in the change of the spin transition frequency for adjacent spin levels by $(E_{DDI}/k_B)/S \simeq 6.7$ mK. Sometimes, for simplicity, the DDI is considered as a kind of inhomogeneous broadening. This is an oversimplification, at least for weakly excited states considered here. Rigorous treatment of the Landau-Zener effect at fast sweep with an account of both DDI and true inhomogeneous broadening (random hyperfine fields)[18] shows that these two effects compete with each other, rather than simply add. In the present case, the magnetostatic field smoothly varies along the crystal (if the crystal shape is non-elliptic), so that its change on the unit-cell distance is very small. Thus the DDI as a source of inhomogeneous broadening will be neglected.

The greatest source of inhomogeneous broadening in Mn_{12} is the hyperfine interaction with their own $N_I = 12$ nuclear spins $I = 5/2$. With the hyperfine coupling A between the total electronic spin S and each of the nuclear spins I of $A/k_B = 2$ mK (Ref. 19), the dispersion of the hyperfine field δH_{HF} on the electronic spin is given by[15,20]

$$\delta H_{HF} = \frac{\sqrt{\sigma_I}A}{g\mu_B}, \qquad \sigma_I = \frac{N_I}{3}I(I+1), \tag{84}$$

whereas the inhomogeneous line shape is Gaussian. Numerically one obtains $\delta H_{HF} \simeq 8.8$ mT. For the transition between adjacent spin levels for the inhomogeneous broadening $\delta\omega_0$ in Eq. (62) one has $\hbar\delta\omega_0 = g\mu_B\delta H_{HF}$, thus $\hbar\delta\omega_0/k_B \simeq 12$ mK. In another popular compound Fe_8 the inhomogeneous broadening is mainly due to the DDI with nuclear spins of hydrigen atoms present in magnetic molecules, $\delta H \simeq 0.8$ mT according to Ref. 21.

One can see that in Mn_{12} the inhomogeneous broadening 12 mK is smaller than the spin-phonon gap $\hbar\Delta/k_B \simeq 40$ mK in the non-diluted case, thus it can be neglected in the first approximation. On the other hand, as said above, the pure bottleneck case requires dilution below n_S^* of Eq. (79), and for $n_S \lesssim n_S^*$ one has $\delta\omega_0 > \Delta$. For Fe_8 the inhomogeneous broadening begins to play a role for a very strong dilution where measurements are difficult. If the inhomogeneous broadening is dominating, the relaxation is governed by the frequency-interval botleneck parameter $B_{\overline{\omega_0}}$ of Eq. (66). With the help of Eq. (77) one obtains

$$B_{\overline{\omega_0}} = \frac{n_S}{\sqrt{2\pi}}\frac{\pi^2\widetilde{\Omega}_D^3}{\overline{\omega_0}\delta\omega_0}. \tag{85}$$

At the critical dilution this becomes

$$B^*_{\overline{\omega_0}} = \frac{n_S^*}{\sqrt{2\pi}}\frac{\pi^2\widetilde{\Omega}_D^3}{\overline{\omega_0}\delta\omega_0} = \frac{1}{2^{7/2}\pi^{3/2}}\frac{\overline{\omega_0}}{\delta\omega_0} \cong 0.016\frac{\overline{\omega_0}}{\delta\omega_0}. \tag{86}$$

That is, for any line with a well-defined central frequency $\overline{\omega_0}$ the bottleneck parameter is large. With the above parameters for Mn_{12} one obtains $B_{\overline{\omega_0}} \simeq 2\times 10^3\ n_S$, $\overline{\omega_0}/\delta\omega_0 \simeq 1000$, and $B^*_{\overline{\omega_0}} \simeq 16$ that is still large. Then Eq. (73) yields $1 - p_\infty \simeq 0.11$, that is, only a 10% of the initial spin excitation can relax before the bottleneck plateau is reached. Thus the inhomogeneous broadening in Mn_{12} does not fully resolve the PB, and in Fe_8 its effect is even smaller.

X. DISCUSSION

The problem of the phonon bottleneck considered in this paper in the weak-excitation limit is only a part of a larger problem of collective spin-phonon relaxation. The bottleneck in the pure form occurs for magnetically diluted systems that satisfy the condition $k_0 r_0 \gg 1$, where k_0 is the wave vector of a resonant phonon and r_0 is the typical distance between the neighboring spins. If this condition is violated, one cannot consider the phases of emitted phonons reaching other spins as random, and the interference effects become important. The well-known example of interference effects is superradiance[3,12] that requires, among other conditions, a coherent initial condition of spins. In contrast to the bottleneck, superradiance dramatically increases the relaxation rate, so that the two effects should compete. On the other hand, destructive interference effects in the case of incoherent initial condition or dynamical loss of coherence due to the inhomogeneous broadening can lead to suppression of relaxation that resembles the PB but has a different physical origin. For this reason, using the results of this paper to interpret experiments should be done with care as the experimental observations can be a mixture of different effects. In particular, the results obtained in this paper are not applicable to non-diluted molecular magnets.

Considering the weak-excitation limit in this paper allowed to drastically simplify the Schrödinger equation and obtain numerically exact results for the PB effect with and without inhomogeneous broadening of spins and phonon damping. It was confirmed that the bottleneck parameter B quantifying the statistical weights of spins and resonant phonons, introduced in Ref. 11, plays the main role in the problem. Fundamentally the most interesting case corresponds to the pure model without inhomogeneous spin broadening and phonon damping. For this model, similarly to the results of Ref. 11, the spin excitation $p(t)$ was shown to oscillate approaching the

bottleneck plateau, see Fig. **??**. However, these oscillations have a smaller amplitude and are stronger damped than the analytical results of Ref. 11. The frequency of these oscillations corresponds to the gap Δ between the two branches of the hybridyzed magnetoelastic waves at resonance [see Eq. (30) and Fig. **??**]

Here it was shown that the bottleneck parameter effectively decreases in the presence of inhomogeneous broadening that alleviates the bottleneck condition. If the inhomogeneus spin line width $\delta\omega_0$ exceeds the spin-phonon gap frequency $\Delta/\hbar$, the splitting of spin and phonon modes is not resolved and the oscillations of $p(t)$ are washed out, see Fig. 3.

Inclusion of the *ad hoc* phonon relaxation rate $\Gamma_{\rm ph}$ in the theory describes the second, post-plateau, stage of the spin relaxation. An important observation is that for $B \gg 1$ the corresponding relaxation rate is much smaller that $\Gamma_{\rm ph}$ (see Figs. **??** and 4) and the spin relaxation is non-exponential [see Eq. (47) and Fig. **??**]. One should stress, however, that it is not completely satisfactory to plug an *ad hoc* phonon relaxation into the theory. The latter should be treated in this case as taken from the experiment. This can lead to a problem since one of the main sources of the observed phonon damping can be their scattering on spins that is already taken into account by the very spin phonon interaction, Eq. (4). On the other hand, this and other kinds of elastic scattering cannot help the system to reach complete equilibrium since these processes conserve the energy and do not transfer excitation from the narrow group of resonant phonons to the rest of the phonon bath.

It would be of a principal importance to generalize the theory of phonon bottleneck for the higly excited initial states of the spin subsystem. However, the Schrödinger equation in this case is not amenable to a direct numerical solution. In Ref. 12 it was argued that, since collective motion of spins in the regions large in comparizon to the typical distance between the neighboring spins involves a large number of atomic spins, the problem can be considered classically. Thus the spin and phonon operators in Eqs. (9) and (10) of Ref. 12 had been replaced by classical variables. This gives a possibility to numerically treat highly excited states of the spin-phonon system without the combinatorial explosion of the full SE. On the other hand, linearization of the classical equations of motion of Ref. 12 near the ground state yields equations that are equivalent to the truncated SE, Eq. (7), in the low-excitation limit. This suggests that classical equations Ref. 12 are indeed a good approximation for the spin-phonon problem in the whole energy range. It would be interesting to investigate what are the quantum corrections to these equations.

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